

2

OFFICE OF NAVAL RESEARCH

AD-A236 000



Contract N00014-85-K-0631

R&T Code 413r005

Technical Report No. UWIS/DC/TR-91/4

Photoluminescence Studies of Silver-Exchanged Cadmium Selenide Crystals. Modification of a Chemical Sensor for Aniline Derivatives by Heterojunction Formation.

by

Larry K. Leung,^a Norma J. Komplin,^a Arthur B. Ellis,^{*,a} and Ned Tabatabaie^{*,b}

Prepared for Publication in the
Journal of Physical Chemistry

^aUniversity of Wisconsin
Department of Chemistry
Madison, Wisconsin 53706

^bUniversity of Wisconsin
Department of Electrical and Computer Engineering
Madison, Wisconsin 53706

DTIC
ELECTE
JUN 03 1991
S B D

May 20, 1991

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.

*To whom all correspondence should be addressed

91-00860



91 5 30 008

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION NA			1b RESTRICTIVE MARKINGS NA		
2a SECURITY CLASSIFICATION AUTHORITY NA			3 DISTRIBUTION AVAILABILITY OF REPORT Distribution Unlimited; Approved for Public Release		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE NA					
4 PERFORMING ORGANIZATION REPORT NUMBER(S) UWIS/DC/TR-91/4			5 MONITORING ORGANIZATION REPORT NUMBER(S) NA		
6a NAME OF PERFORMING ORGANIZATION Chemistry Department University of Wisconsin-Madison		6b OFFICE SYMBOL (If applicable) NA	7a NAME OF MONITORING ORGANIZATION ONR		
6c ADDRESS (City, State, and ZIP Code) 1101 University Avenue Madison, WI 53706			7b ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217		
8a NAME OF FUNDING/SPONSORING ORGANIZATION		8b OFFICE SYMBOL (If applicable) NA	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-85-K-0631		
8c ADDRESS (City, State, and ZIP Code)			10 SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO	TASK NO
11 TITLE (Include Security Classification) Photoluminescence Studies of Silver-Exchanged Cadmium Selenide Crystals. Modification of a Chemical Sensor for Aniline Derivatives by Heterojunction Formation					
12 PERSONAL AUTHOR(S) Larry K. Leung, ^a Norma J. Komplin, ^a Ned Tabatabaie, ^b and Arthur B. Ellis ^a (^a UW-Madison Chemistry Dept., ^b UW-Madison Electrical and Computer Engineering Dept.)					
13a TYPE OF REPORT Technical	13b TIME COVERED FROM _____ TO _____		14 DATE OF REPORT (Year, Month, Day) 2/1/91		15 PAGE COUNT 44
16 SUPPLEMENTARY NOTATION Prepared for publication in the Journal of Physical Chemistry					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) cadmium selenide; silver selenide; time-resolved photoluminescence; picosecond spectroscopy; carrier dynamics; aniline sensor; CdSe/Ag ₂ Se heterojunction		
FIELD	GROUP	SUB-GROUP			
19 ABSTRACT (Continue on reverse if necessary and identify by block number) Single-crystal n-CdSe surfaces have been modified by an exchange reaction with aqueous Ag ⁺ that converts part of the surface to Ag ₂ Se and releases Cd ²⁺ to solution. Formation of Ag ₂ Se is established by X-ray powder diffraction. ESCA and Auger spectroscopy are consistent with the formation of Ag ₂ Se islands having thicknesses of ~20-500 Å, depending on reaction conditions. Steady-state photoluminescence (PL) experiments show that Ag ⁺ -exchanged CdSe (CdSe/Ag ⁺) can be superior to CdSe as an aniline sensor: ring-substituted aniline derivatives in toluene solution cause enhancements of the CdSe band edge PL in CdSe/Ag ⁺ samples relative to a toluene ambient, with the effect about twice as large as for unexchanged CdSe. The variations in PL intensity of CdSe/Ag ⁺ are well fit by a dead-layer model, allowing estimation of the adduct-induced change in depletion width. The magnitude of these variations in depletion width for CdSe/Ag ⁺ can approach 1000 Å. The affinity of the aniline derivatives for the CdSe/Ag ⁺ surfaces, as estimated from the fit of concentration-dependent PL changes to the Langmuir adsorption isotherm model, is also about twice that of unexchanged CdSe.					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Distribution Unlimited		
22a NAME OF RESPONSIBLE INDIVIDUAL Arthur B. Ellis			22b TELEPHONE (Include Area Code) (608) 262-0421		22c OFFICE SYMBOL

Abstract

Single-crystal n-CdSe surfaces have been modified by an exchange reaction with aqueous Ag^+ that converts part of the surface to Ag_2Se and releases Cd^{2+} to solution. Formation of Ag_2Se is established by X-ray powder diffraction. ESCA and Auger spectroscopy are consistent with the formation of Ag_2Se islands having thicknesses of $\sim 20\text{-}500$ Å, depending on reaction conditions. Steady-state photoluminescence (PL) experiments show that Ag^+ -exchanged CdSe (CdSe/Ag^+) can be superior to CdSe as an aniline sensor: ring-substituted aniline derivatives in toluene solution cause enhancements of the CdSe band edge PL in CdSe/Ag^+ samples relative to a toluene ambient, with the effect about twice as large as for unexchanged CdSe. The variations in PL intensity of CdSe/Ag^+ are well fit by a dead-layer model, allowing estimation of the adduct-induced change in depletion width. The magnitude of these variations in depletion width for CdSe/Ag^+ can approach 1000 Å. The affinity of the aniline derivatives for the CdSe/Ag^+ surfaces, as estimated from the fit of concentration-dependent PL changes to the Langmuir adsorption isotherm model, is also about twice that of unexchanged CdSe: equilibrium constants are about $60\text{-}300 \text{ M}^{-1}$ for the binding of several aniline derivatives to CdSe/Ag^+ . Time-resolved PL

decay curves of the CdSe edge emission of CdSe/Ag⁺ samples demonstrate that the rate of carrier recombination increases with the extent of the exchange reaction, eventually saturating. PL decay curves of CdSe/Ag⁺ are insensitive to adduct formation for *p*-OCH₃ and *p*-CH₃ derivatives, suggesting that the surface recombination velocity is not greatly affected by aniline adsorption. An isotype heterojunction model for the CdSe/Ag₂Se interface is proposed to rationalize these observations.



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

INTRODUCTION

We have recently demonstrated that the photoluminescence (PL) of semiconductors can be perturbed reversibly by the adsorption and desorption of molecules from gas and solution phases, permitting exploitation of the solids as on-line chemical sensors. The basis for this effect is hypothesized to be an adsorption-induced shift in the distribution of surface states relative to the band edges and in the electronic occupancy of the states, thereby altering the depletion width W . If W is assumed to be a nonemissive zone, as a result of efficient separation of photogenerated carriers (a "dead-layer" model), the PL intensity will be affected, a result we have verified quantitatively (vide infra) for numerous adducts of molecules with semiconductor surfaces.¹⁻⁷

In designing sensors using these principles, we have found that classical coordination chemistry is an excellent guide to predicting what adducts are likely to form between molecules and surface atoms. Striking PL effects have been obtained by using CdSe surfaces to detect amines, reflecting the avidity with which Cd^{2+} ions bind to the $-\text{NH}_2$ functionality. Moreover, use of a family of aniline compounds yielded broadly tunable PL responses: control of electron density at the coordination site was achieved by varying the ring substituent.⁷

In this paper we demonstrate that the PL response of CdSe to aniline derivatives may be amplified by exchanging the surface with aqueous Ag^+ ions, as indicated in eq. 1. This chemical displacement



reaction has ample precedent in the preparation of $\text{Cu}_2\text{Se/CdSe}$,⁸ $\text{Cu}_2\text{S/CdS}$,⁹ and $\text{Ag}_2\text{S/CdS}$ ¹⁰ heterojunctions. We provide evidence from surface analytical techniques that our synthetic method creates Ag_2Se islands that decorate the surface with n-CdSe/n- Ag_2Se isotype heterojunctions. Steady-state and temporal PL data reveal that these heterojunctions enhance the binding affinity of aniline derivatives for the surface; increase carrier recombination kinetics; and enhance the initial band bending, causing larger aniline-induced changes in PL intensity and depletion width relative to unexchanged CdSe surfaces, and making the silver-exchanged solids (CdSe/Ag^+) superior chemical sensors for aniline derivatives.

EXPERIMENTAL

Materials and Methods. Single-crystal, vapor-grown, c-plates of n-CdSe, resistivity $\sim 2 \Omega\text{-cm}$, were obtained from Cleveland Crystals, Inc.

The crystals were etched in Br_2/MeOH (1:30 by volume; 5s), revealing the shiny, Cd-rich (0001) face, which was excited in the PL experiments. All the anilines ($p\text{-OCH}_3$, $p\text{-CH}_3$, -H) were at least 98% pure as purchased from Aldrich and were distilled in vacuo or sublimed before use. Toluene (Baker) was purged with N_2 . Solutions were stored in a N_2 glove bag and used within 48 h. Bulk Ag_2Se was made from a stoichiometric melt of 0.732 g Ag (Aldrich; 99.999%) and 0.268 g Se (Aldrich; 99.999%); the reagents were heated at 1000°C for ~ 12 h in an evacuated quartz ampoule, cooled to 650°C , where annealing took place for several hours, and then cooled to room temperature.¹¹ Films of Ag_2Se were prepared by evaporation of bulk Ag_2Se at 5×10^{-5} torr onto chromium-coated glass substrates held at room temperature in a Mo boat. Film thicknesses, determined by profilometry using a Tencor Instruments Model Alpha-Step 200, were used to calibrate sputtering rates for Auger spectroscopy experiments.

Exchange Experiments. Solutions were prepared from AgNO_3 (EM Science) and Millipore water and kept in the dark until use. For steady-state PL studies, samples of n-CdSe were cut to $\sim 8 \times 4 \times 2 \text{ mm}^3$ and etched. Before exchange, half the crystal surface was coated with nail polish so that it could be compared with the modified surface. Exchange reactions

were typically conducted by dipping the crystal in 5 μM AgNO_3 solution for 15 min. in the dark. Crystals were rinsed in acetone to dissolve the nail polish and ultrasonicated in methanol. The reaction was often monitored by the decline in bulk PL of the crystal, which was held by Duco cement on the end of a glass rod and dipped into a glass cell initially containing Millipore water. When the water was drained and replaced by a 5 μM AgNO_3 solution, the PL declined over several minutes to ~50% of its initial intensity at which time the AgNO_3 solution was drained, and the crystal was rinsed with Millipore water. For temporal PL experiments, crystals were cut to $\sim 4 \times 4 \times 2 \text{ mm}^3$, and exchange was effected by exposure to either 5 μM or 5 mM AgNO_3 solutions for varying lengths of time.

Surface Characterization. X-ray powder diffraction data were obtained on exchanged CdSe powder (Aldrich; 99.99+%). Typically, 1.0 g of the powder was slurried in 20 mL of a 0.2 M AgNO_3 aqueous solution in the dark. The solid was removed by filtration after 30 min., rinsed with deionized water and air dried. X-ray data were obtained on a Nicolet R3m/V Polycrystalline X-ray Diffraction System using $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectra were obtained using a Perkin Elmer Model 5400 ESCA system, with Ag and Ag_2Se as standards. Auger electron spectroscopy was performed using a Perkin Elmer Model 660 Scanning

Auger Mutiprobe and calibrated using the Ag_2Se film standards. Different areas on the surface were surveyed to give an average depth profile. To examine photoinertness of the exchanged surfaces, a picosecond laser beam (250 mW at 587 nm) was focused to a 1-mm diameter point and crudely rastered over the crystal surface continuously for 2 hours. X-ray photoelectron spectra taken on the irradiated area before and after photolysis showed no Ag peaks other than those due to Ag_2Se .

Steady-State Optical Measurements. The sample cell and the experimental setup have been described.⁴ Samples were excited with a Coherent Innova 90-5 Ar^+ laser (457.9 and 514.5 nm) or a Melles-Griot Model 80 He-Ne laser (632.8 nm). PL intensity was continuously monitored at the PL band maximum (a recorder was used in time-base mode), as the solution was varied. The cell was drained and the PL recorded in pure toluene after each measurement in aniline solution.

Time-Resolved Optical Measurements. Excitation was provided by a Coherent Antares Nd-YAG laser system, as previously described.⁵ Using rhodamine 6G, the dye laser of the system produces a 2-ps pulse (FWHM) with an average power of 250 mW at 587 nm. The beam was focused to a ~0.2-mm diameter point on the crystal, yielding an output of $\sim 10^{20}$ photons/cm³/pulse. PL decay profiles, measured at room temperature, were analyzed by time-correlated single photon

counting;^{1 2} the instrument response function was ~50 ps. Fits of data were performed to the Kohlrausch form, using a modification of the program CURFIT by Bevington.^{1 3} The PL decay curves were iteratively reconvoluted from the instrument response function.

RESULTS AND DISCUSSION

In sections below we describe the physicochemical properties of the CdSe/Ag⁺ interface; steady-state PL properties used to estimate adduct-induced changes in depletion width and adduct formation constants; time-resolved PL data; and a model to account for the observed data.

Surface Studies. The exchange reaction shown in eq. 1 is effected by slurrying CdSe powder in aqueous AgNO₃ solution. As Fig. 1 reveals, the CdSe peaks present in the starting material are joined by others in the reaction product that match naumannite, Ag₂Se.^{1 4}

When a single crystal of CdSe is used, the photoelectron spectrum of the exchanged solid likewise shows a match with data reported for Ag₂Se.^{1 5} Specifically, the binding energy of the Ag 3d_{5/2} level at 367.9 eV is observed and shifted, as reported, relative to a Ag metal standard.^{1 5, 1 6} It is noteworthy that surfaces of exchanged crystals

appear to be photoinert under the experimental conditions of our PL measurements, since Ag_2Se appeared to be the only Ag-containing species present in the photoelectron spectra before and after irradiation.

Auger electron spectroscopy (AES) coupled with Ar^+ sputter etching provides a depth profile of the exchanged material. A typical depth profile, shown in Fig. 2a, reveals a monotonic increase in Cd and decrease in Ag concentrations, from the surface to the bulk. The thickness of the Ag_2Se film was estimated as being the distance at which the atomic concentration of Ag^+ in the bulk has dropped to half of its surface value. This estimate is only an approximation, however, since the sputtering rate is obtained from thin films of Ag_2Se , whereas the exchanged surfaces appear to be mixtures of Ag_2Se and CdSe . Samples like that shown in Fig. 2a that were exchanged for short times with low concentrations of AgNO_3 , exhibited depth profiles that varied markedly with surface position, suggesting that the Ag_2Se phase is nonuniformly distributed over the surface. Similar observations had been made in previous studies.^{10b} In contrast, exposure of CdSe crystals to ~ 1 mM AgNO_3 solutions for 5 min. produces Auger spectra having no Cd^{2+} on the surface, indicative of complete Ag_2Se surface coverage, Fig. 2b.

Dead-Layer Model Results. We have estimated adsorption-induced

changes in the depletion width W of CdSe and of CdSe/Ag⁺ by steady-state PL measurements through use of a dead-layer model. The model assumes that a region of thickness D , on the order of the depletion width, is nonemissive, or "dead" insofar as PL is concerned, because the photogenerated electron-hole pairs are swept apart by the electric field and cannot recombine to yield PL.¹⁷

The quantitative form of the dead-layer model that we employ for CdSe- and CdSe/Ag⁺-aniline interfaces is given by eq. 2,

$$PL_{ref}/PL_x = \exp(-\alpha'\Delta D) \quad (2),$$

where PL_{ref} is the PL intensity in a toluene reference solvent; PL_x is the PL intensity in a toluene solution of an aniline derivative; $\alpha' = (\alpha + \beta)$ is the absorptivity of the semiconductor, corrected for self-absorption; and $\Delta D = (D_{ref} - D_x)$ is the difference in the dead-layer thickness in passing from pure solvent to aniline solution. Operationally, we check for applicability of the model by use of different interrogating excitation wavelengths: eq. 2 predicts different PL ratios but a constant value for ΔD as absorptivity is varied.

Use of the dead-layer model assumes that the surface recombination velocity S is either insensitive to adsorption or relatively

large in both ambients [$S \gg L_p / \tau_p$ and $S \gg \alpha L_p^2 / \tau_p$, where τ_p and L_p are the minority carrier (hole) lifetime and diffusion length, respectively].¹⁸

In conducting steady-state PL experiments, we found that the red, band edge PL of CdSe ($E_g \sim 1.7$ eV; 720 nm) is observable only under reaction conditions leading to limited exchange; we restricted ourselves to reaction conditions that, from Auger data, correspond to Ag_2Se thicknesses of ~ 20 Å. Excitation intensities were typically ~ 1 mW/cm².

In order to assess the effects of Ag^+ exchange directly, we studied two halves of a sample surface, one half of which had been immersed in AgNO_3 solution to prepare a CdSe/ Ag^+ interface. Each half of the solid was excited separately with ultra-bandgap light while immersed in toluene solvent or in toluene aniline solutions; the liquids are easily changed without altering the sample-detection optics geometry. We have focused on *para* substituents to minimize the steric effects on surface binding.⁷

Like other amines, aniline causes an enhancement in the PL intensity of CdSe and of CdSe/ Ag^+ relative to solvent. The PL changes are reversible and concentration dependent, saturating by ~ 0.2 M for both systems. Figure 3 shows the PL changes of CdSe and CdSe/ Ag^+ upon adsorption of the anilines. For CdSe, the magnitude and direction of the

changes in PL intensity have been correlated with the adsorbates' Hammett substituent constants, a measure of the electron density at the coordination site.^{7,19}

For CdSe/Ag⁺, the same qualitative shift is observed: aniline adsorption increases the PL intensity relative to the toluene solvent with the effect enhanced as the ring substituent becomes more electron donating. But, for a given aniline derivative, the magnitude of the PL enhancement is roughly twice as large from the CdSe/Ag⁺ half of the sample as from the CdSe half. We have observed this effect using four different samples.

For both exchanged and unexchanged samples, the changes in PL intensity caused by aniline adsorption are well fit by the dead-layer model: Fig. 4 shows that a constant ΔD value is obtained for each aniline derivative using three excitation wavelengths. The ΔD values correspond to the maximum reduction in dead-layer thickness induced by aniline adsorption and reach values of 700-900 Å for the aniline derivatives on the CdSe/Ag⁺ surface. We should note that we did not modify the dead-layer model for use with the CdSe/Ag⁺ surface, since the layer thicknesses were small and the surface coverage incomplete (vide supra).

The larger changes in the dead-layer thickness from the exchanged surfaces prompted us to investigate the relative magnitude of the pre-adsorption band bending between CdSe and CdSe/Ag⁺. Previous studies of the CuS/CdS²⁰ and InSb/GaAs²¹ heterojunctions have shown that junction formation increases the band bending at the interface. To investigate this effect in CdSe/Ag⁺, intensity studies have been carried out.

Increasing the incident light intensity should reduce the pre-adsorption value of D and, therefore, the adduct-induced reductions in D. We have investigated the intensity dependence of the PL ratio of CdSe and CdSe/Ag⁺ with *p*-CH₃ aniline using 514.5-nm light. The studies show that for CdSe, the maximum PL ratio, measured for the *p*-CH₃ derivative, is constant over ~1 to 12 mW/cm²; as the intensity increases beyond this point, the PL ratio starts to decline, consistent with a pre-adsorption state with a smaller electric field thickness.⁷ In contrast, the maximum PL ratio of CdSe/Ag⁺ remains constant over a larger intensity range of between ~1 to 25 mW/cm², at which point it begins to drop. This observation is consistent with the notion that a larger pre-adsorption band bending exists near the surface of the

exchanged CdSe/Ag⁺ solid compared to CdSe.

Adduct Formation Constants. Equilibrium constants for adduct formation between the adsorbate and CdSe(/Ag⁺) surfaces can be estimated from the concentration dependence of the PL changes using the Langmuir adsorption isotherm model.^{1-7,22} The quantitative form of the model is given by eq. 3,

$$\theta = KC / (1 + KC) \quad \text{or} \quad 1/\theta = 1 + 1/(KC) \quad (3),$$

where θ is the fractional surface coverage, K is the equilibrium constant, and C is the solution concentration of the adsorbate; a double-reciprocal plot of θ^{-1} vs. C^{-1} should be linear with a slope equal to K^{-1} .

We assumed that the maximum PL changes correspond to maximum surface coverage ($\theta = 1$). If θ is taken to be the fractional change in ΔD , which from eq. 2 is proportional to $\ln (PL_x/PL_{ref})$, we obtain eq. 4:^{6,7}

$$\theta = \ln [PL_x/PL_{ref}] / \ln [PL_{sat}/PL_{ref}] \quad (4),$$

where PL_{ref} , PL_{sat} , and PL_x correspond to the reference ($\theta = 0$), saturated ($\theta = 1$), and intermediate PL intensities.

Figure 5 presents the adsorption isotherms of the *p*-CH₃ aniline derivative for CdSe and CdSe/Ag⁺ surfaces. The data are well fit by the Langmuir adsorption isotherm model. The Fig. 5 data show that the

equilibrium constant for CdSe/Ag^+ is roughly twice that of CdSe , an observation we made on all of the samples tested. We also constructed adsorption isotherms for the $p\text{-OCH}_3$ derivative and for aniline itself and found a similar, approximate doubling of K in passing from the unexchanged to the exchanged surface. Fig. 6 summarizes the data for a particular sample. The approximate doubling of K following Ag^+ exchange is a relatively modest effect compared to the 300-fold higher binding constant of Ag^+ for aniline in water compared to Cd^{2+} .²³ This suggests that the PL response to aniline is still dominated by the binding at Cd^{2+} sites, although perhaps perturbed by the presence of Ag_2Se on the surface.

Time-Resolved Experiments. In conducting time-resolved experiments, we examined PL decay profiles of crystals of $n\text{-CdSe}$ before and after exchange with Ag^+ ions. Decay profiles, $I(t)$, were nonexponential and well fit by the two-parameter Kohlrausch function, eq. 5,^{5,24}

$$I(t) = I_0 \exp [-(t/\tau_k)^{\beta_k}] \quad (5)$$

The parameter β_k ($0 < \beta_k < 1$) has been related to a distribution of exponential decay times that are serially linked

(β_k is sometimes referred to as a "width parameter"; as β_k becomes smaller, the distribution becomes broader), and the parameter τ_k , the lifetime, is the time at which the relaxation function $I(t)$ falls to I_0/e and corresponds to the maximum in the distribution of the decay times. Figure 7 demonstrates the goodness-of-fit of the PL decay profile to the Kohlrausch equation. An average relaxation time, $\langle\tau_k\rangle$, has also been defined.^{24b,25}

Figure 8 shows the different decay profiles of CdSe/Ag⁺ crystals, exchanged to varying degrees. The corresponding average film thicknesses from AES/Ar⁺ sputter etch data and the Kohlrausch parameters of each crystal are summarized in Table I. The data in the table indicate that as the extent of exchange increases, β_k , τ_k , and $\langle\tau_k\rangle$ decrease, eventually reaching limiting values and reflecting a significant perturbation of carrier recombination processes in the solid.

Qualitatively, the trends in τ_k and $\langle\tau_k\rangle$ indicate that Ag⁺/Cd²⁺ exchange increases the number and/or influence of sites of fast nonradiative decay, presumably through introduction of defect states. Recent studies have shown that metals such as Ag, Au, and Cu can cause lattice dissociation of the CdS and CdSe surfaces and create lattice defects and dangling bonds.^{20,26} Besides the defect states that might be

associated with isolated Ag^+ centers, the interface states at the $\text{CdSe}/\text{Ag}_2\text{Se}$ heterojunction can act as effective recombination centers with large capture cross-sections for minority carriers (holes).^{20,27}

The β_k parameter is ~ 0.6 in CdSe and its decline with Ag^+ exchange appears to saturate at ~ 0.5 . The broadening of the dispersion in decay sites may be linked to the nonuniform distribution of Ag_2Se islands on the surface of CdSe inferred from our Auger/ Ar^+ sputter etch data (vide supra).

Under the strong illumination conditions used in our experiments, $\sim 10^{19}$ - 10^{20} photons/ cm^3 /pulse, band flattening should occur, meaning that the Ag^+ -induced temporal PL changes are driven by changes in the surface recombination velocity S and not by changes in W . Huppert et al. have used similar experimental conditions to conclude that other exchanging ions like Cu^{2+} cause S for CdS and CdSe to increase.²⁰

A major assumption of the dead-layer model is that S is either very high in both toluene solvent and aniline solution, or unaffected by the solution environment. Temporal experiments were undertaken to seek evidence for adduct-induced changes in recombination kinetics. We find, however, that the luminescence decay profiles for both CdSe and CdSe/Ag^+ in toluene are unaffected by *p*-methoxy- and *p*-methylaniline

adsorption. This is the case both at moderate intensity and also at high intensity where the bands should be more nearly flat. The fact that the decay profiles are insensitive to aniline adsorption implies that either S is unchanged by adsorption or that our technique is unable to detect changes in S that may be occurring.

An Interfacial Orbital Interaction Model. The CdSe/Ag₂Se interface can be regarded as an abrupt n-n heterojunction. The crystal structures and lattice constants of Ag₂Se and CdSe are quite different, leading to a large lattice mismatch. Irrespective of the preparation method,¹¹ Ag₂Se has been found to be an n-type semiconductor with a monoclinic structure at room temperature; the semiconductor is characterized by a high carrier density (10^{17} - 10^{19} cm⁻³) and a bandgap energy of 0.07 eV. Because of the abrupt change in the structure of the lattice (CdSe has the wurtzite structure), interface states are likely to form, as mentioned earlier. These interface states, besides affecting S , as inferred from the temporal PL data (vide supra), can also increase the initial (pre-adsorption) band bending.^{20,21,27} Our intensity studies have shown that a stronger incident light intensity is required to induce the intensity effects for CdSe/Ag⁺ compared to CdSe, consistent with a

larger initial band bending in CdSe/Ag⁺. Figure 9 highlights the importance of surfaces and interface states on the energy band profiles of CdSe and Ag₂Se/CdSe. In Fig.9(a), a positively charged depletion region exists near the surface of n-CdSe, due to the trapping of negative charge, presumably by the unsaturated surface Cd²⁺ ions. We hypothesize the presence of a broad distribution of surface states that straddles the Fermi level.⁷

The electronic occupancy of these surface states can be reduced by the presence of interface states at the abrupt n-n heterojunction, Fig. 9(b), leading to a larger depletion width, as inferred from our intensity studies. Similar band profiles to that shown in Fig. 9(b) have been proposed for the CuS/CdS^{20c} and GaAs/InSb²¹ heterojunctions. It is noteworthy that charge neutrality in CdSe/Ag⁺ is no longer maintained on an axial basis but is, of course, for the overall volume.

The interaction of the dipolar aniline species with the surface Cd sites can be likened to the formation of a weak donor-acceptor complex, Fig.10.⁷ As shown in Fig.10(a), the donor HOMO and acceptor LUMO are slightly stabilized and destabilized, respectively, by the formation of the complex, but there is little transfer of charge density between them; accordingly, the complex is readily dissociated. The analogous picture

for aniline adsorption onto CdSe can be represented in Fig.10(b). In this case, the surface states may interact with the aniline HOMO to produce a new distribution that can lead to a reduction in depletion width by raising the energies of the surface states closer to the conduction band and reducing their overall electronic occupancy.

The analysis of our experimental results, based on the dead layer model, suggests the following possible scenario for the case of CdSe/Ag⁺, shown in Fig.10(c). The figure shows a larger initial depletion layer and lower electronic occupancy in the surface states of the bare CdSe region, presumably due to the trapping of electrons by the neighboring Ag₂Se. It is thus likely that a similar shift of the Fermi energy, resulting from aniline adsorption, spans a region of larger density of surface states as compared with untreated CdSe. Consequently, this new equilibrium state results in a greater amount of charge having been transferred from localized surface states into the bulk semiconductor and leads to a larger change in the depletion width.

Acknowledgements

We thank the Office of Naval Research for generous support of this work. We are also grateful to Dr. Ngoc Tran for helpful discussions.

References

1. Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1988**, 110, 4914.
2. Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. *Anal. Chem.* **1988**, 60, 2531.
3. Meyer, G. J.; Leung, L. K.; Yu, J. C.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1989**, 111, 5146.
4. Murphy, C. J.; Ellis, A. B. *J. Phys. Chem.* **1990**, 94, 3082.
5. Leung, L. K.; Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. *J. Phys. Chem.* **1990**, 94, 1214.
6. Lisensky, G. C.; Penn, R. L.; Murphy, C. J.; Ellis, A. B. *Science* **1990**, 248, 840.
7. Murphy, C. J.; Lisensky, G. C.; Leung, L. K.; Kowach, G. R.; Ellis, A. B. *J. Am. Chem. Soc.* **1990**, 112, 8344.
8. Komashchenko, V. N.; Kynev, S.; Marchenko, A. I.; Fedorus, G. A. *Ukr. Fiz. Zh.* **1968**, 13, 2086.
9. (a) Russell, G. J.; Oktik, S.; Woods, J. *J. Mat. Sci. Lett.* **1983**, 2, 229. (b) Cheng, C. H.; Jones, K. A. *J. Electrochem. Soc.* **1980**, 127, 1375. (c) Schlesener, C. J.; Streckert, H. H.; Ellis, A. B. *Anal. Chem.* **1981**, 53, 2283.
10. (a) Mulder, B. J. *J. Cryst. Growth* **1974**, 23, 214. (b) Bruzzoni, P.; Jutter, K. *Electrochim. Acta* **1984**, 29, 1665.

11. (a) Damodara, V. D; Karunakaran, D. *Phys. Rev. B* **1989**, 39, 10872.
(b) Constantinescu, L. V. *Rev. Roum. Phys.* **1980**, 26, 1123. (c)
Constantinescu, L. V. *Rev. Roum. Phys.* **1983**, 28, 73.
12. O'Connor, D. Z.; Phillips, D. In *Time-Correlated Single Photon Counting*; Academic Press: New York, 1985.
13. Bevington, P. R. In *Data Reduction and Error Analysis for Physical Sciences*; McGraw-Hill: New York, 1969.
14. The X-ray powder diffraction pattern is obtained from JCPDS file #25-766.
15. Romand, M.; Roubin, M.; Deloume, J. P. *J. Electron Spectrosc. Relat. Phenom.* **1978**, 13, 229.
16. Wagner, C. D.; Riggs, W. M.; Davis, L.E.; Moulder, J. F.; Muilenberg, G. *E. Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, Minnesota, 1979.
17. (a) Hollingsworth, R. E.; Sites, J. R. *J. Appl. Phys.* **1982**, 53, 5357.
(b) Ellis, A. B. In *Chemistry and Structure at Interfaces: New Laser and Optical Techniques*; Hall, R. B., Ellis, A. B. VCH Publishers: Deerfield Beach, FL, 1986; Chap. 6.
18. (a) Mettler, K. *J. Appl. Phys.* **1977**, 12, 75. (b) Burk, A. A., Jr.; Johnson, P. B.; Hobson, W. S.; Ellis, A. B. *J. Appl. Phys.* **1986**, 59, 1621.

19. Lowry, T. H.; Richardson, K. S. In *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper & Row: New York, 1981; pp130-145.
20. (a) Benjamin, D.; Huppert, D. *J. Phys. Chem.* **1988**, 92, 4676. (b) Rosenwaks, Y.; Burstein, L.; Shapira, Y.; Huppert, D. *Appl. Phys. Lett.* **1990**, 57, 458. (c) Rosenwaks, Y.; Burstein, L.; Shapira, Y.; Huppert, D. *J. Phys. Chem.* **1990**, 94, 6842.
21. Hinkley, E. D.; Rediker, R. H.; Jadus, D. K. *Appl. Phys. Lett.* **1965**, 6, 144.
22. (a) Laidler, K. J. In *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987, p 230. (b) Dannhauser, T.; O'Neil, M.; Johansson, K.; Whitten, D.; McLendon, G. *J. Phys. Chem.* **1986**, 90, 6074.
23. (a) Smith, R. M.; Martell, A. E. In *Critical Stability Constants*, Plenum Press: New York, 1975; Vol. 2, p. 8. (b) Nazarova, L. V.; Ablov, A. V.; Dagaev, V. A. *Russ. J. Inorg. Chem.* **1964**, 9, 1150. (c) Smith, R. M.; Martell, A. E. In *Critical Stability Constants*, Plenum Press: New York, 1975; Vol. 5, p. 133. (d) M'Foundou, E.; Berthon, G. *Analusis* **1973**, 2, 658.
24. (a) Palmer, R. G.; Stein, D. L.; Abrahams, E.; Anderson, P. W. *Phys. Rev. Lett.* **1984**, 53, 958. (b) Linsey, C. P.; Patterson, G. D. *J. Chem. Phys.* **1980**, 73, 3348. (c) Alivisatos, A. P.; Arndt, M. F.; Efrima, S.; Waldeck, D. H.; Harris, C. B. *J. Chem. Phys.* **1987**, 86,

6540. (d) O'Neil, M.; Marohn, J.; McLendon, G. *J. Phys. Chem.* **1990**, 94, 4356.

25. According to Lindsey and Patterson (ref 24b), if $I(t)$ is considered as arising from a superposition of exponentials (a distribution of decay profiles), eq. 5 may be written as

$$\exp [-(t/\tau_k)^{\beta_k}] = \int_0^{\infty} \exp(-t/\tau) \rho_k(\tau) d\tau \quad (i)$$

which defines the Kohlrausch distribution function $\rho_k(\tau)$. In general, it is possible to find the average relaxation time, $\langle \tau_k \rangle$, without explicit knowledge of $\rho_k(\tau)$:

$$\langle \tau_k^n \rangle = \int_0^{\infty} \tau^n \rho(\tau) d\tau = \{1/\Gamma(n)\} \int_0^{\infty} t^{n-1} I(t) dt \quad (ii)$$

where $\Gamma(n)$ is the gamma function. Equation (ii) may now be used to define the average relaxation time $\langle \tau_k \rangle$,

$$\langle \tau_k \rangle = (\tau_k / \beta_k) \Gamma(1/\beta_k) \quad (iii)$$

26. (a) Brucker, C. F.; Brillson, L. J. *J. Vac. Sci. Technol.* **1981**, 18, 787. (b) Brucker, C. F.; Brillson, L. J. *J. Vac. Sci. Technol.* **1981**, 19, 617.
27. (a) Oldham, W. G.; Milnes, A. G. *Solid-State Electron.* **1963**, 6, 121. (b) Oldham, W. G.; Milnes, A. G. *Solid-State Electron.* **1964**, 7, 153. (c) Tersoff, J. *Phys. Rev. Lett.* **1984**, 52, 465.
28. Absorptivities for CdSe are found in: Parsons, R. B.; Wardzynski,

W.; Yoffe, A. D. *Proc. R. Soc. London, A* 1961, 262, 120.

Table I. Average film thicknesses and PL-derived Kohlrausch parameters of CdSe and CdSe/Ag⁺ crystals.

Solid ^a	Film thickness (Å) ^b	β_k ^c	τ_k (ps) ^c	$\langle\tau_k\rangle$ (ps) ^d
(a) CdSe	- -	0.56±0.01	150±10	250±20
(b) CdSe/Ag ⁺	20±5	0.51±0.01	71±6	140±10
(c) CdSe/Ag ⁺	37±5	0.50±0.01	43±5	86±9
(d) CdSe/Ag ⁺	50±5	0.46±0.01	23±3	46±6
(e) CdSe/Ag ⁺	280±10	0.46±0.01	23±3	46±6

^a Samples of CdSe and CdSe/Ag⁺ crystals, labeled (a) to (e), yielded the decay profiles shown in Fig. 8. The exchange conditions for the CdSe/Ag⁺ crystals are as follows: (a) no exchange; (b) 5 μ M AgNO₃ for 15 min.; (c) 5 μ M AgNO₃ for 30 min.; (d) 5 μ M AgNO₃ for 60 min.; and (e) 5 mM AgNO₃ for 5 min.

^b Average film thicknesses of Ag₂Se in CdSe/Ag⁺ samples, determined from AES/Ar⁺ sputtering experiments, as described in the text.

^c Parameters β_k and τ_k , obtained from the Kohlrausch equation (eq. 5 in

the text) by averaging data from three trials.

^d Values of the average relaxation time $\langle \tau_k \rangle$ were calculated from equation (iii) in ref 25.

Figure Captions

Figure 1. X-ray powder diffraction patterns for CdSe (top) and CdSe/Ag⁺ (bottom). The CdSe/Ag⁺ powder was obtained by slurring 1.0 g of CdSe powder in 20 mL of a 0.2 M AgNO₃ aqueous solution in the dark. In the bottom panel, the additional peaks (indicated by the arrows) match those of Ag₂Se (see ref 14).

Figure 2. Depth profiles of CdSe/Ag⁺ crystals obtained from AES/Ar⁺ sputtering experiments. Part (a) corresponds to an average film thickness of 37 ± 5 Å and (b) to an average thickness of 280 ± 10 Å. The atomic concentrations of the elements are not corrected for the different sensitivity factors of the individual elements. The Ar⁺ sputtering rate was estimated to be 60 Å/min. Concentrations of Cd, Ag, and Se were obtained by monitoring the peak intensities at 376 eV, 351 eV, and 1315 eV, respectively. The CdSe/Ag⁺ crystal of (a) was obtained by exchange with a 5 µM AgNO₃ solution for 30 min. and the crystal of (b) by exchange with a 5 mM AgNO₃ solution for 5 min.

Figure 3. Relative changes in PL intensity at 720 nm resulting from exposure of a n-CdSe sample (left half of the figure) and a CdSe/Ag⁺ sample (right half) to toluene (initial response) and to a ~0.2 M solution of the indicated aniline derivative in toluene. The data were measured

from two halves of the same CdSe sample, with one half exchanged with a 5 μM AgNO_3 solution for 15 min. and the other half unmodified.

Superimposed on the plot are the PL spectra of the CdSe and CdSe/ Ag^+ samples, obtained in toluene and normalized to a common intensity (the CdSe/ Ag^+ signal is about 3 times weaker than that of CdSe). Downward spikes are caused by the draining of the cell under N_2 when the solutions were changed. The samples were excited with 457.9-nm light in all cases.

Figure 4. Maximum values of ΔD , $\pm 10\%$, for a CdSe sample (left) and a CdSe/ Ag^+ sample (right) with each of the aniline derivatives examined, calculated with eq. 2 of the text. The data were determined from the two halves of the same sample as in Fig.3. Typical aniline concentrations needed to produce the maximum PL changes were ~ 0.2 M for both samples. Excitation wavelengths in nm are shown in the legend. Penetration depths ($1/\alpha$ of 570, 740, and 1500 \AA at 457.9, 514.5, and 632.8 nm, respectively) and the correction for self-absorption ($\beta = 1.2 \times 10^4 \text{ cm}^{-1}$) were obtained from ref 28.

Figure 5. Plots of the fractional surface coverage θ , defined by eq 4, vs. *p*-methylaniline concentration for a CdSe sample (open circle) and a CdSe/ Ag^+ sample (triangles). The double-reciprocal plots are shown as

insets; linearity implies that the fits to the Langmuir model are good for both cases. Values of K , calculated from eq. 3, were $50 \pm 5 \text{ M}^{-1}$ for CdSe and $90 \pm 10 \text{ M}^{-1}$ for CdSe/Ag⁺. The samples were excited with 457.9-nm light. The data were determined for the two halves of the same sample as in Fig.3.

Figure 6. Calculated values of the adsorption equilibrium constant (eq.3 in the text), $K \pm 10\%$, for the interaction of the indicated amines with single samples of CdSe (left) and CdSe/Ag⁺ (right). The data were determined for the two halves of the same sample as in Fig.5.

Figure 7. Luminescence decay from a CdSe/Ag⁺ sample (estimated average Ag₂Se film thickness of $\sim 20 \pm 5 \text{ \AA}$) in air with 587-nm excitation at an estimated average power of $\sim 250 \text{ mW}$. The dashed curve is the fit to the Kohlrausch equation. The fit parameters are $\beta = 0.51 \pm 0.01$ and $\tau = 71 \pm 6 \text{ ps}$.

Figure 8. Decay profiles of CdSe and CdSe/Ag⁺ crystals, exchanged to varying degrees, measured in air with 587-nm excitation at an estimated average power of $\sim 250 \text{ mW}$. Curve (a) corresponds to the profile of the CdSe crystal and curves (b)-(e) to that of the CdSe/Ag⁺ crystals with increasing coverage of Ag₂Se. Curve (f) is the instrument response function. All curves have all been normalized to a common

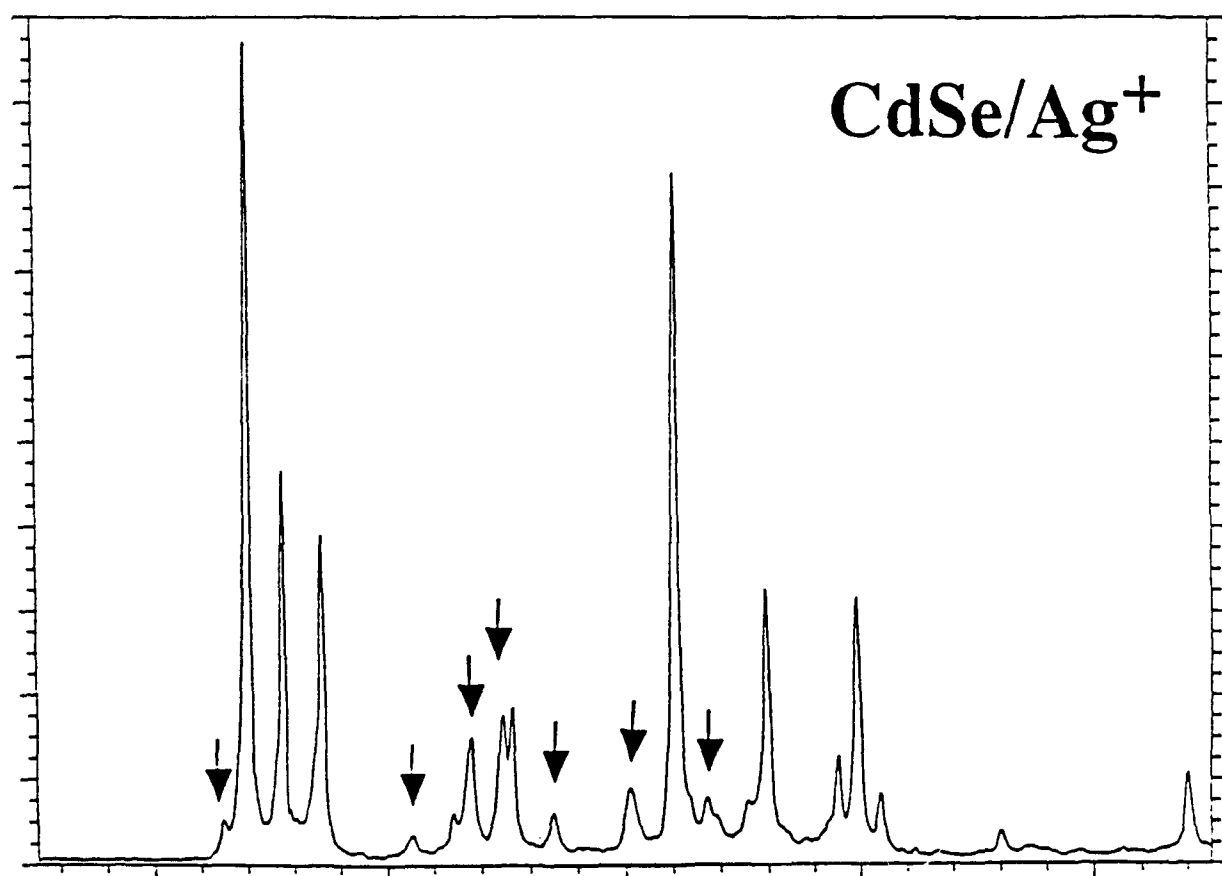
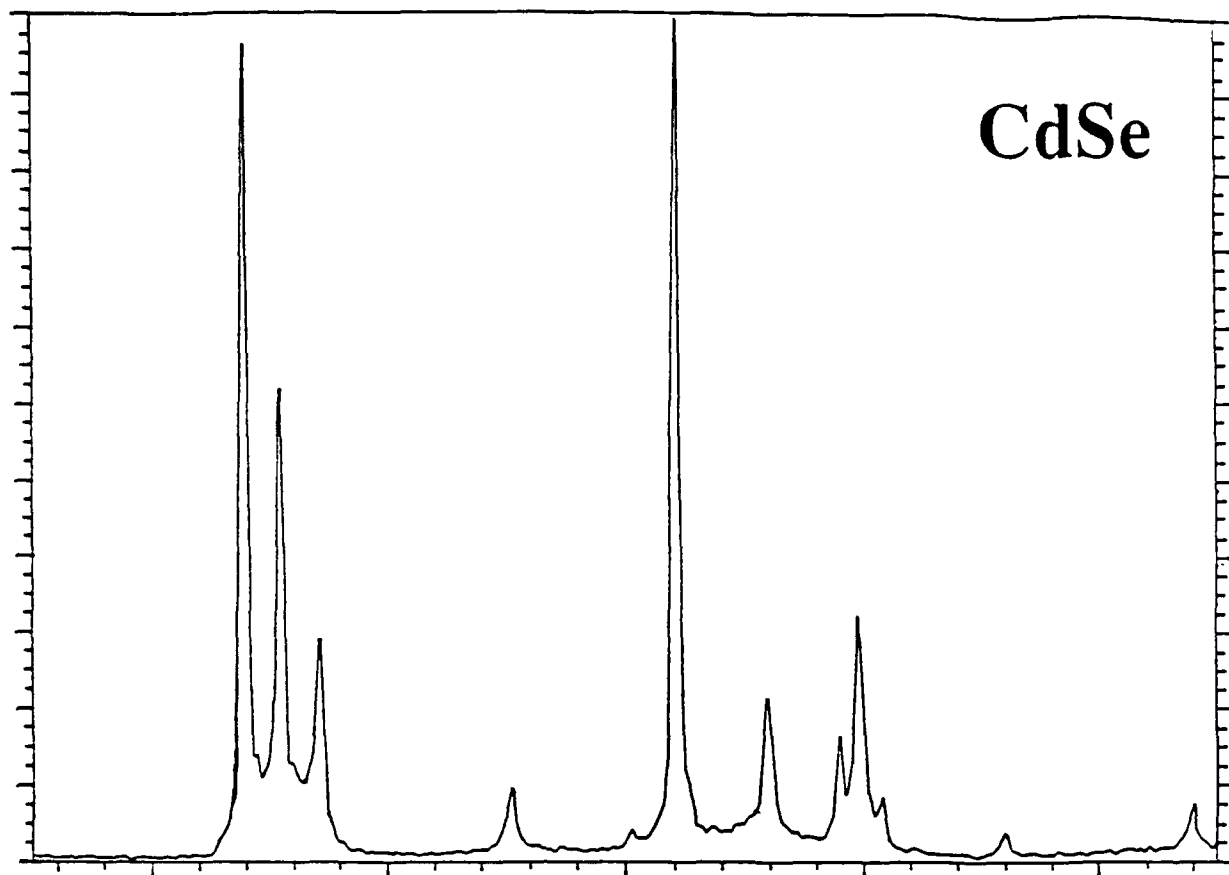
maximum intensity. The corresponding average film thickness from AES/ Ar^+ sputtering experiments, exchange conditions, and the Kohlrausch parameters of each crystal are summarized in Table 1.

Figure 9. Schematic energy band profiles of (a) etched n-CdSe and (b) a CdSe/ Ag_2Se (CdSe/ Ag^+) n-n heterojunction. Part (a) shows a positively charged depletion region existing near the surface of the crystal. The density of surface states is pictured as a distribution about the Fermi level, E_f . Shaded portions of the distribution correspond to occupied surface states. Part (b) illustrates the CdSe/ Ag_2Se heterojunction. We infer from PL intensity effects (see text) that the band bending is increased by the interface states created by the heterojunction.

Figure 10. (a) Molecular orbital formation involving a donor-acceptor pair; the donor's HOMO is slightly stabilized, while the acceptor's LUMO is slightly destabilized. (b) The analogous orbital picture for the interaction of n-CdSe surface states with an aniline donor. The donor's HOMO is slightly stabilized, while the surface states are slightly raised in energy relative to the conduction band edge. (c) A possible scenario for the orbital interaction of the bare CdSe regions of CdSe/ Ag^+ with an aniline donor. Larger changes in the depletion region result from aniline adsorption, presumably reflecting a similar shift in Fermi energy, but

one which now spans a region having a larger density of surface states relative to the untreated CdSe surface in (b).

Intensity



20

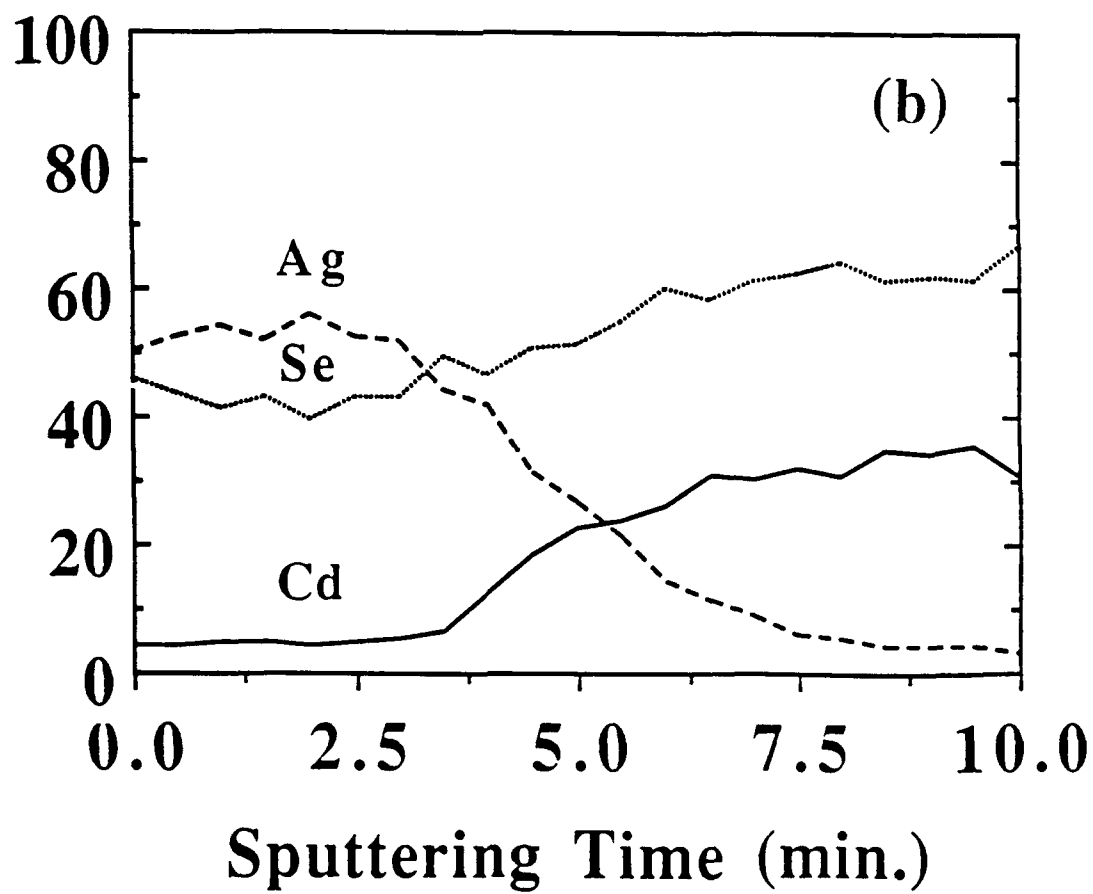
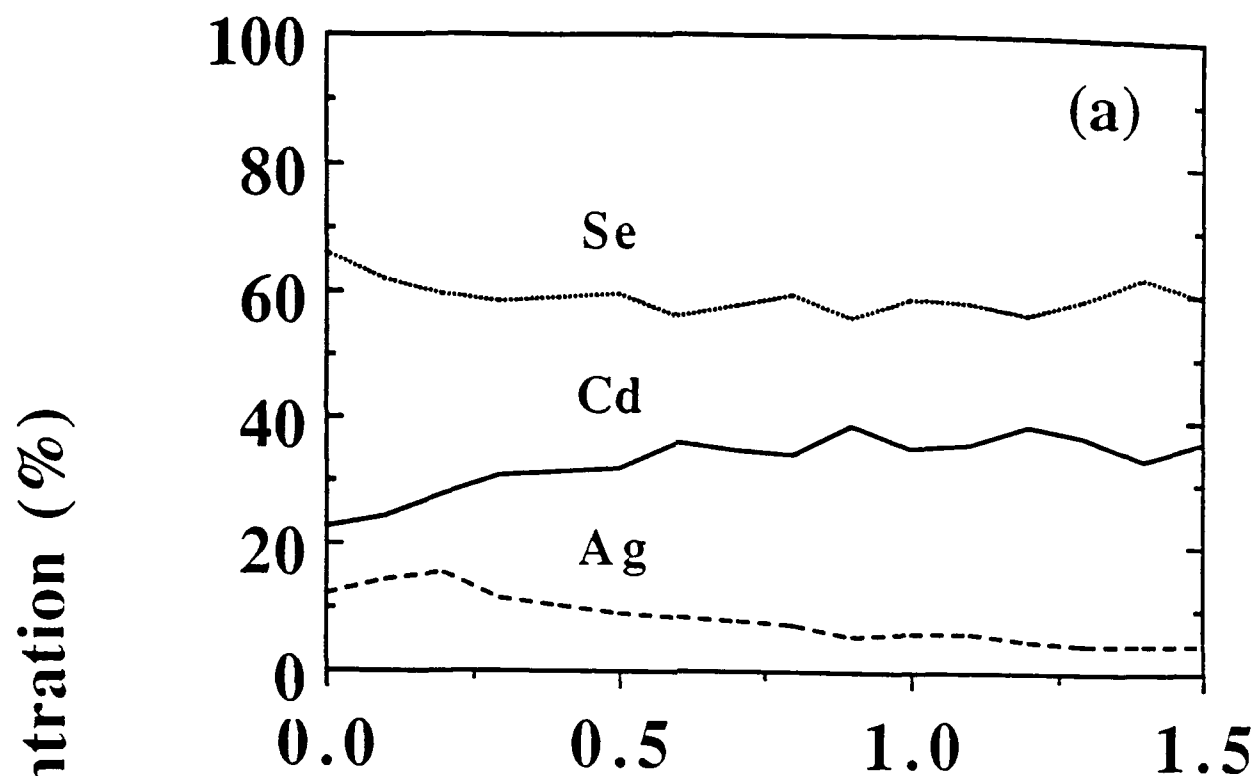
30

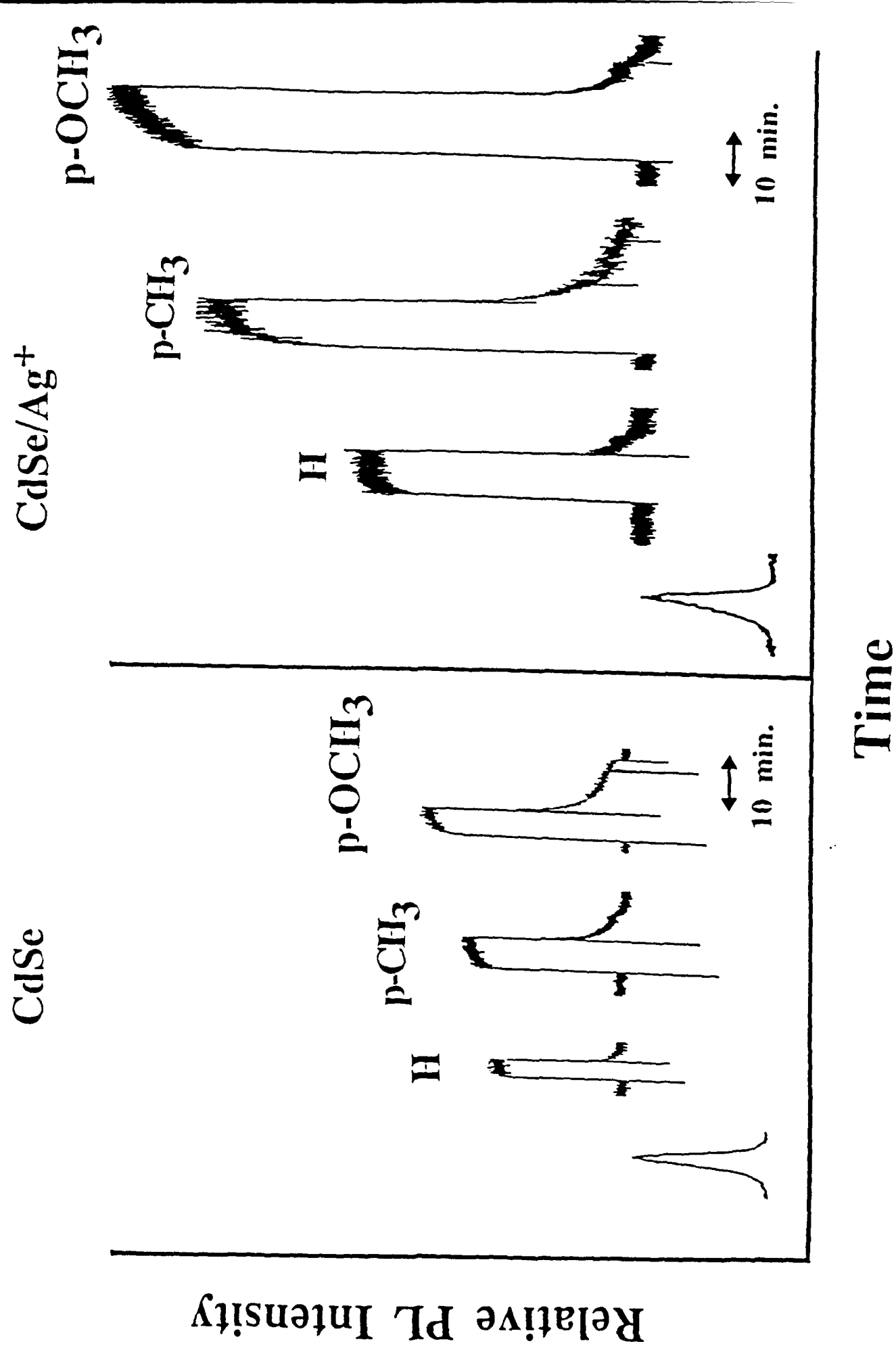
40

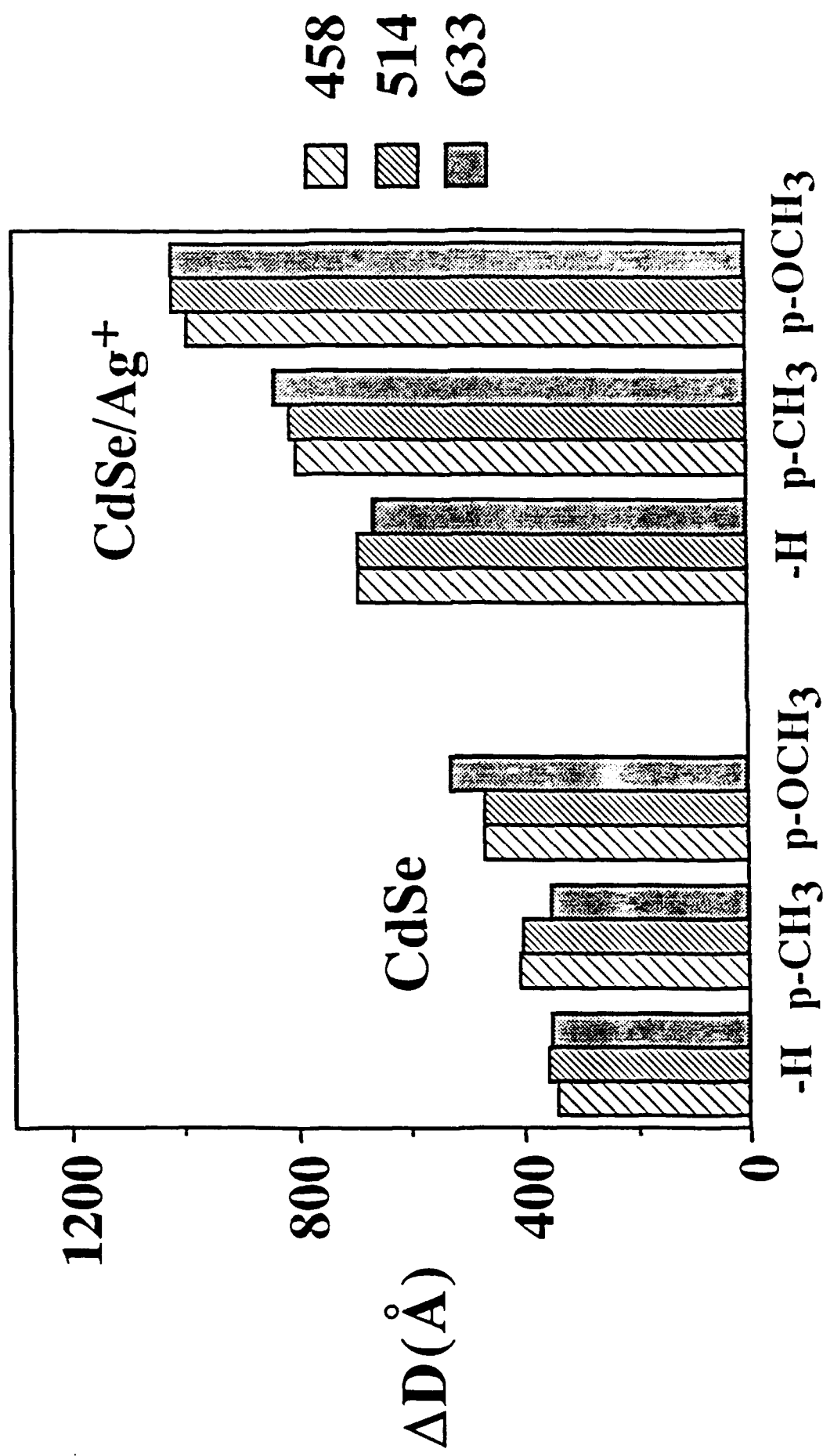
50

60

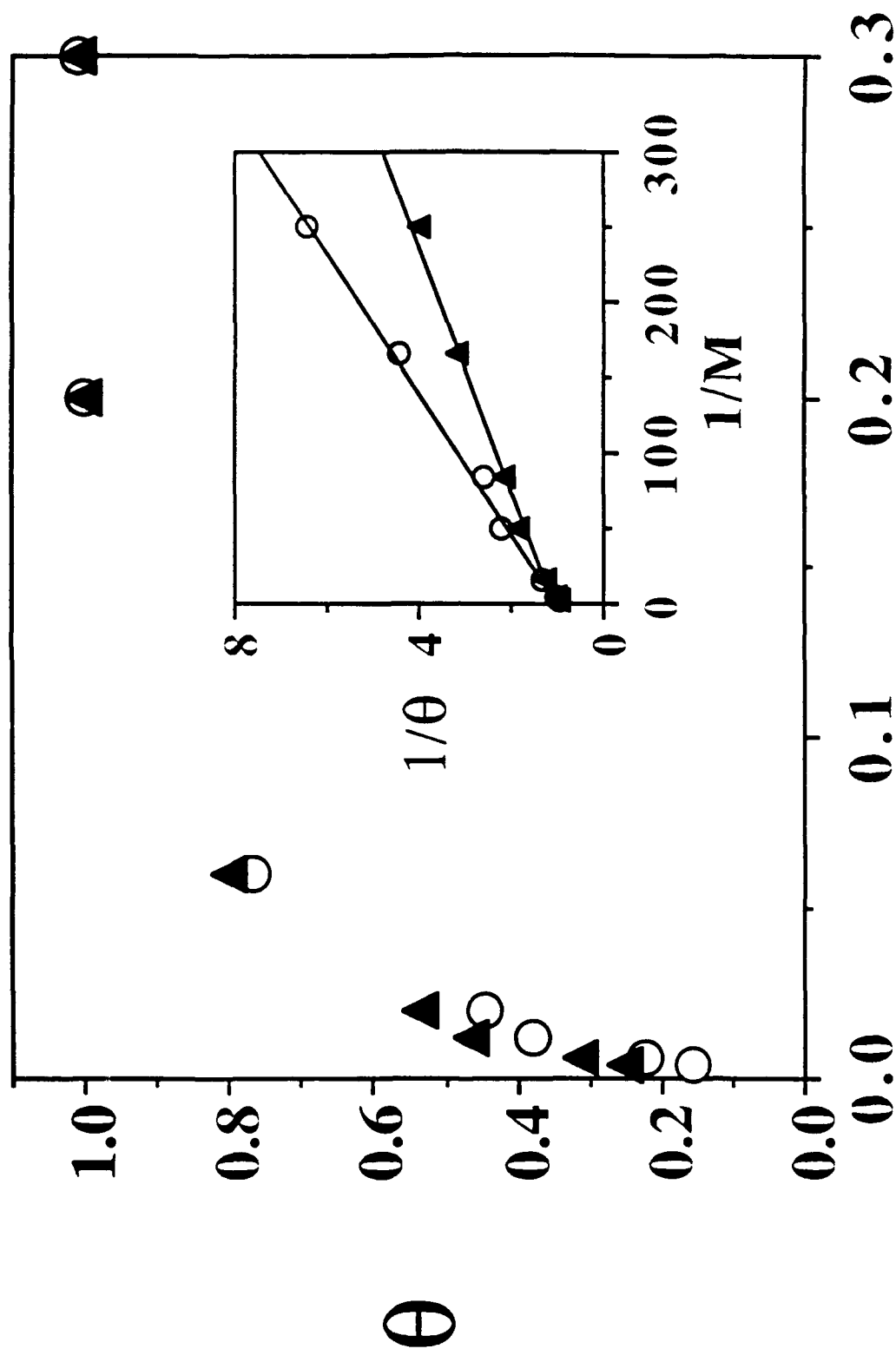
Two-Theta



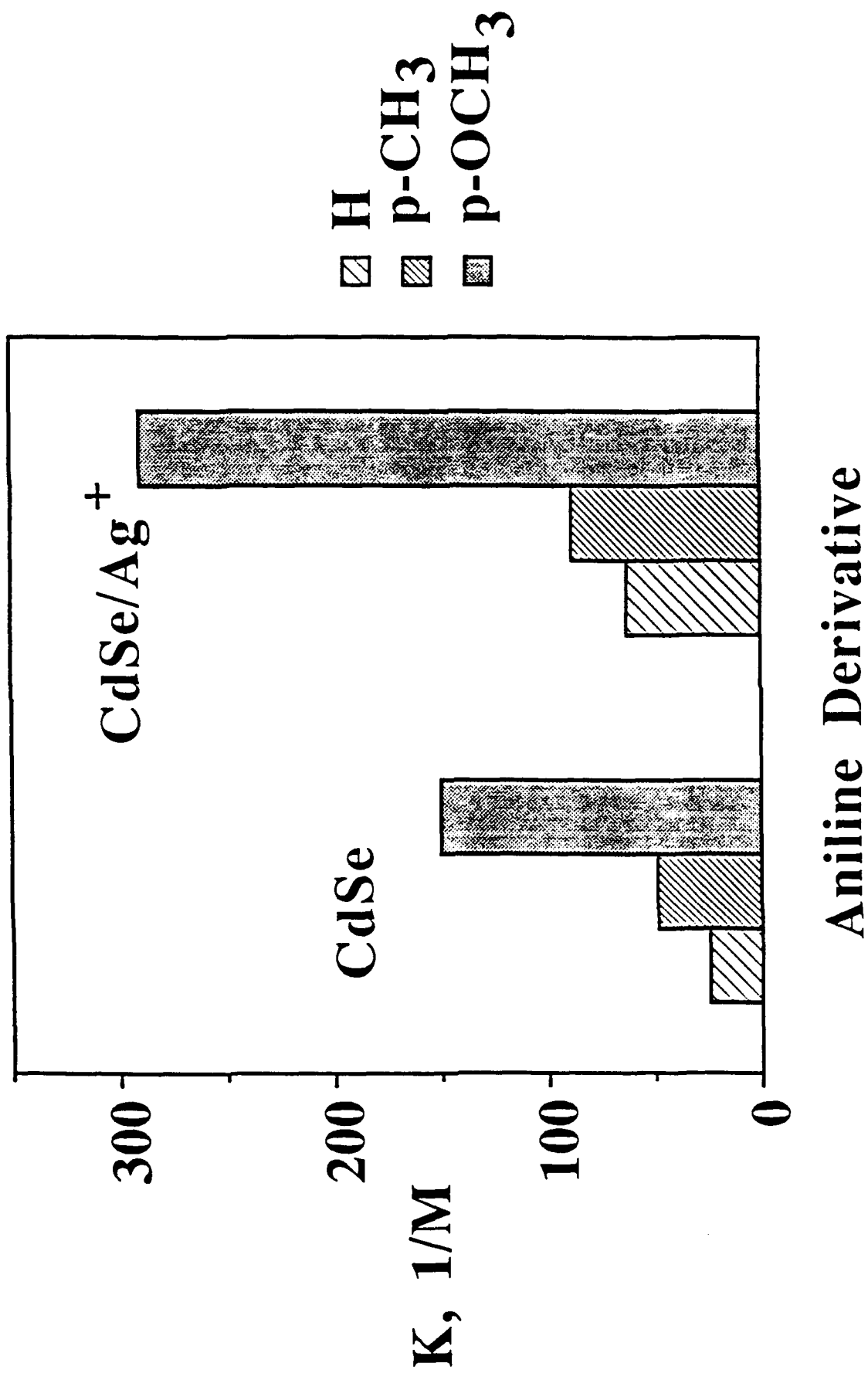


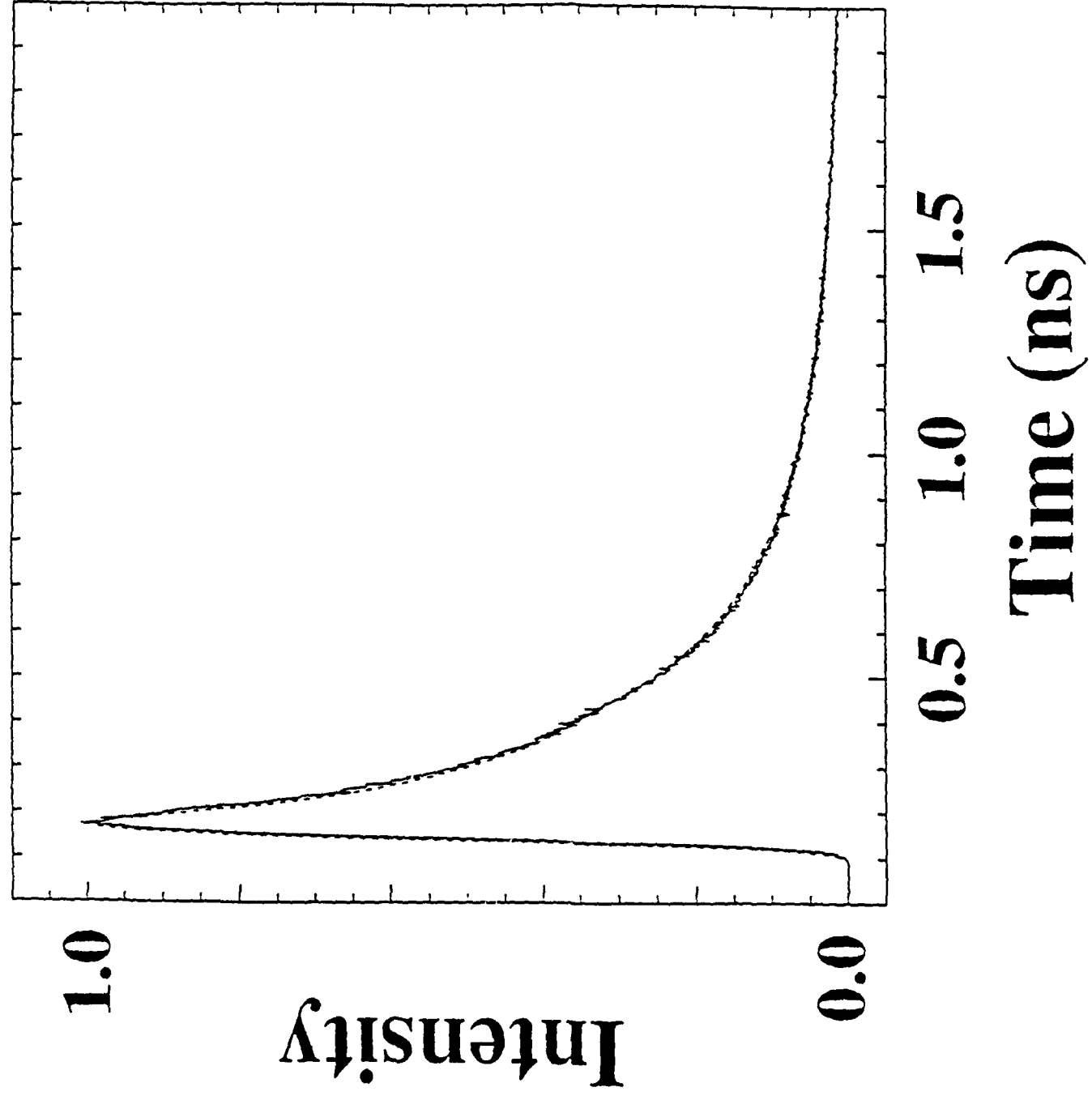


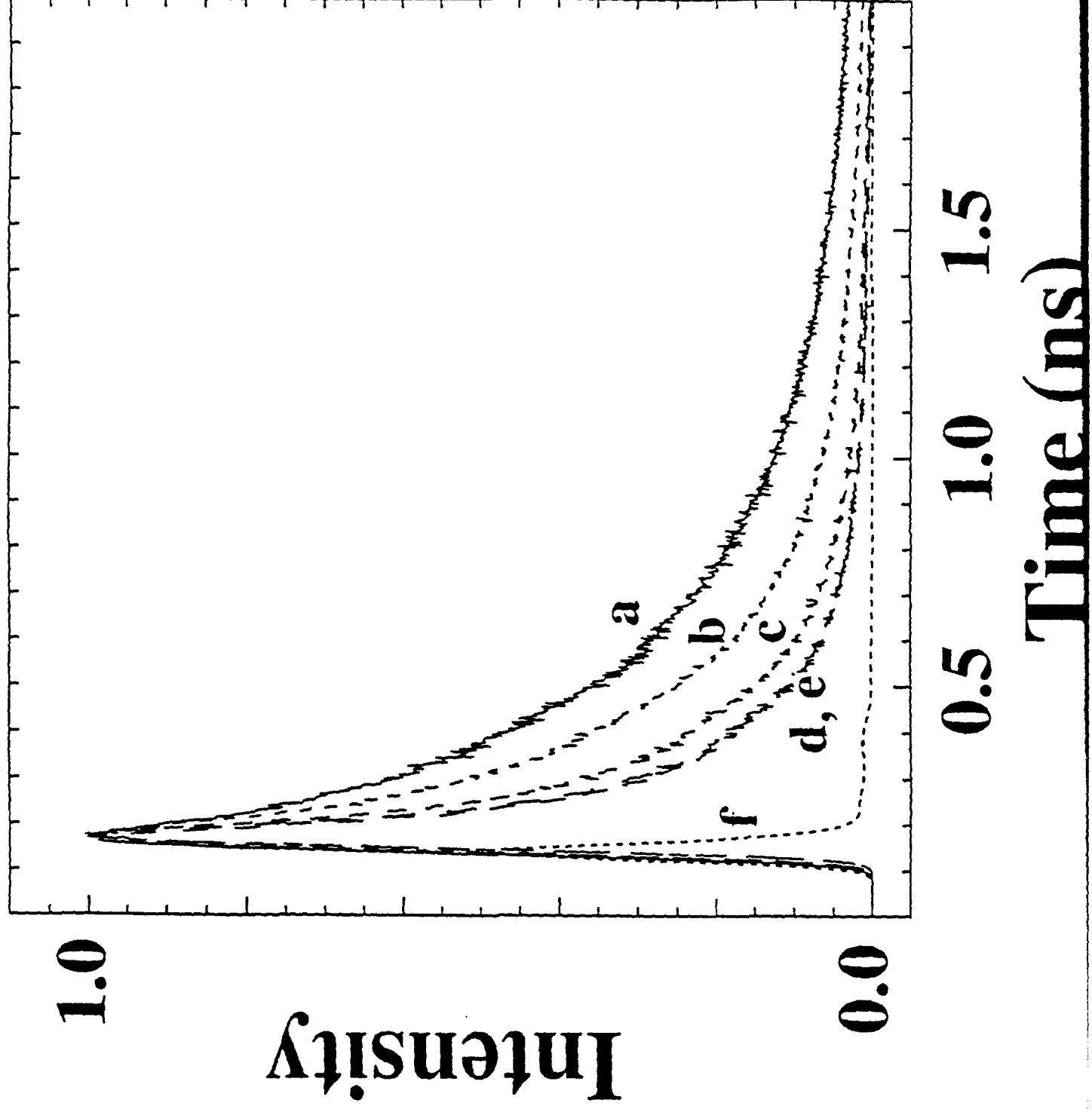
Aniline Derivatives



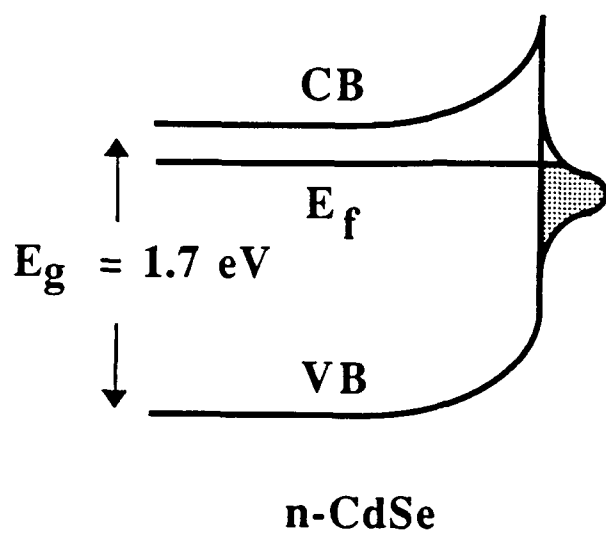
[p-methylaniline], M



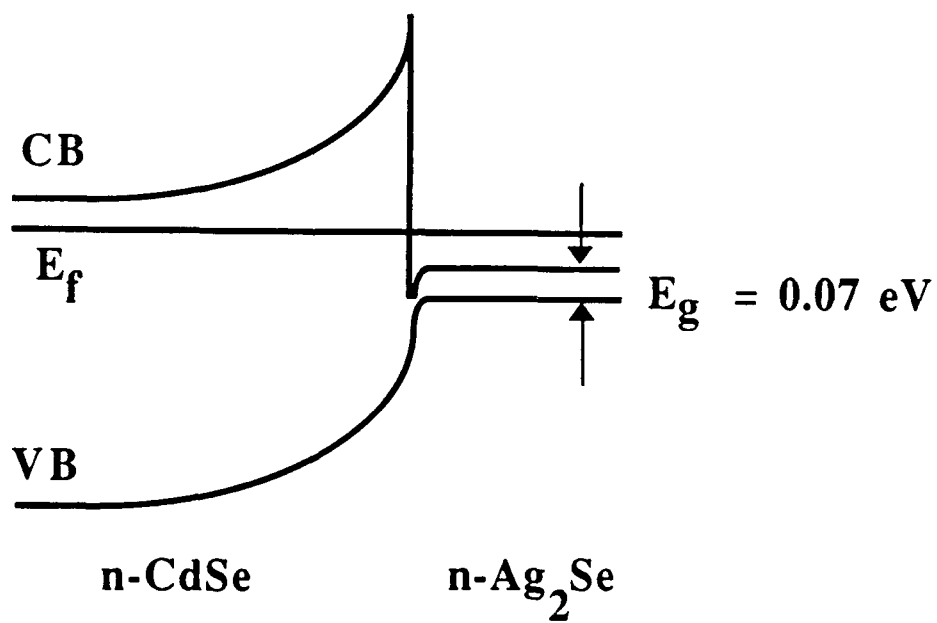




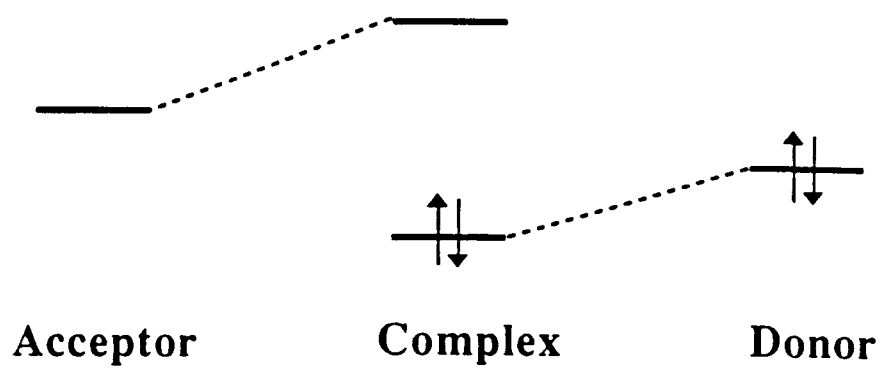
(a)



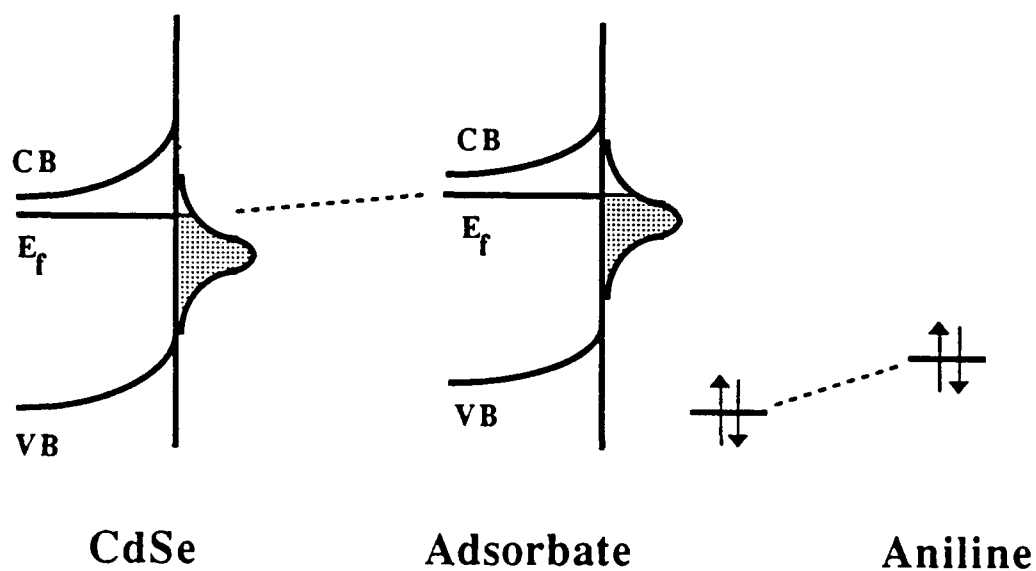
(b)



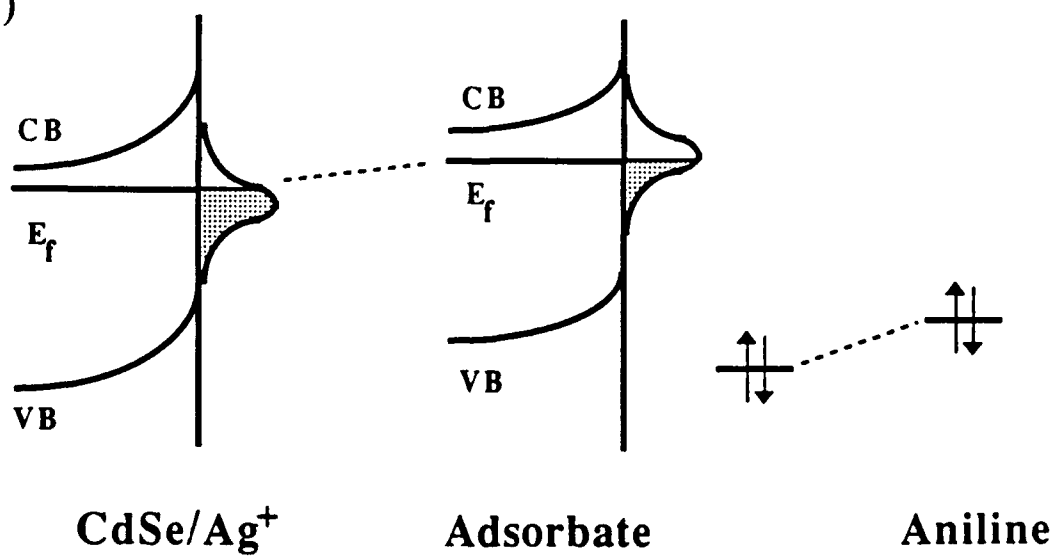
(a)



(b)



(c)



TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Eugene C. Fischer (1)
Code 2840
David Taylor Research Center
Annapolis, MD 21402-5067

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Dr. Elek Lindner (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Doua
Crane, Indiana 47522-5050

* Number of copies to forward